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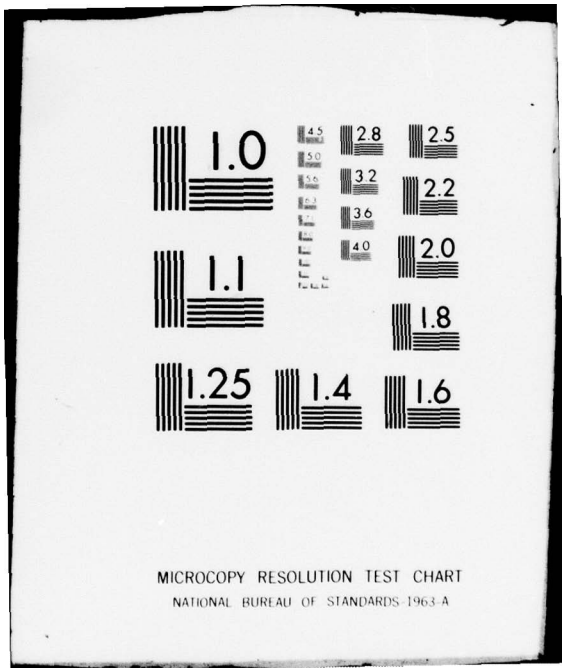
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(2) LEVEL III

INSTABILITY AND FAR-FROM-EQUILIBRIUM STATES OF CHEMICALLY REACTING SYSTEMS

Interim Scientific Report

to

Air Force Office of Scientific Research

by

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February 1979

This Interim Scientific Report covers the period December 1, 1977 to December 1, 1978.

1. Hydrodynamic and Reactive Instabilities

The temperature gradient imposed on a fluid in a gravitational field leads, under suitable conditions, to the onset of convective instability. We have studied the hydrodynamic stability of stationary and oscillatory convection of binary fluids in which both the Soret and Dufour effects are included. Previous work has justifiably neglected these effects in liquids but they are of importance in gases. We use the Boussinesq approximation for a Bénard geometry and find a variational principle for the critical Rayleigh number necessary for the onset of stationary convection. Instability may occur if the system is heated from below or from above. We next drive integral expressions for the critical Rayleigh number necessary for the onset of oscillatory convections. We also obtain expressions for the amplitude of convective and oscillatory motion which depends on the Nusselt number. These expressions are then used to determine the ranges of conditions in which heat flux measurements may be used in the study of instability in binary fluids and the determination of transport coefficients. This work has been submitted to the journal, The Physics of Fluids (Refs. 150, 151).†

†Starred items on the Publication List acknowledge AFOSR research support. Grant no. AFOSR-77-3214

2. Stability and Relative Stability in Reactive Systems Far from Equilibrium

In previously reported work we investigated this problem by two independent methods. The first consisted of a thermodynamic approach in which we assumed that the entropy of the system under consideration is a maximum at any given time for the given constraints of chemical concentrations at that time. With that postulate we obtain a thermodynamic equation of motion from which we derive necessary and sufficient conditions for stability, marginal stability, and obtain a postulate of relative stability of stationary states. The other approach is based on a stochastic theory in which we use the concept of mean first passage time for transition from one to the other of two stable stationary states. We showed that for a one-variable kinetic system the two approaches lead to the same prediction of relative stability (see Publications 126, 127). It is important to test both approaches for two or more variable kinetic systems and work on this problem is in progress. The formal theory of mean first passage times in multi-variable systems is available; however, much further development is necessary to bring that formal theory to a practical prediction. We are approach- this problem along a number of lines. First we are looking at two-variable systems with multiple time scales which can be reduced to effectively one-variable systems. Secondly, we are investigating the

technique of statistical linearization for the investigation of the nonlinear stochastic equations involved in the problem. Third, we are planning to make numerical calculations and to check both basic theory as well as any approximations used in pushing the formal theory to predictive results.

3. Statistical Mechanics of Stationary States

We have begun an extensive investigation of the formal theory of statistical mechanics of stationary states. We begin with the equation for a large system and show how a part of that large system, called a subsystem, may exist in a quasi, nonequilibrium stationary state. We find that the fluctuations around this nonequilibrium stationary state are qualitatively different from equilibrium fluctuations and from fluctuations calculated with a local equilibrium assumption. There appears coupling between the fluctuations and the macroscopic dissipative fluxes; the coupling is due to breaking of time reversal symmetry. We derive the dynamic structure factor of importance in light scattering for a simple fluid under a temperature gradient and find this factor to consist of three terms: the first is the one predicted by local equilibrium theory and is even in wave vector and frequency; the second term is even in frequency and odd in the wave vector; and the third term is odd both in the wave vector and the frequency. We discuss possible light scattering experiments to measure

the newly predicted effects. The first article on the formal theory has been written and has been submitted to Physical Review (Ref. 144).

4. Theory of Unimolecular Reactions

We use a stochastic theory based on a master equation to calculate the mean first passage time, and hence the rate, for unimolecular decomposition. We thus generalize the work of Montroll and Shuler for diatomic molecules to polyatomic molecules. Nonequilibrium contributions to the reaction rate become important for molecules with few degrees of freedom and for high total energy. We thus establish limits of applicability of 'equilibrium' reaction rate theories, such as the RRKM theory. The equilibrium theory is sufficient if the time scale of reaction is slow compared to the time scale of vibrational relaxation. This work has been published in the Journal of Chemical Physics (Ref. 130).

5. Molecular Beam Research

We are continuing our studies on scattering of Ba + Cl_2. So far we have obtained what we believe to be reliable distributions of positive ions $BaCl^+$ which are formed in this reaction. We have measured both angular and velocity distributions. The corresponding negative ion distributions appear to be affected by stray electrons and further work is necessary to assure consistency of both positive and negative ion

distributions.

6. Chemical Waves

Non-linear reaction mechanisms coupled with transport processes, such as diffusion, may produce chemical waves. We have studied these processes for reaction mechanisms with two time scales, which include the important class of relaxation oscillations. We have studied previously such problems by means of multiple time scale expansions and now have used the lowest order approximation to derive bounds and expressions for the velocity of waves in these systems. The oscillatory chemical reactions studies experimentally so far are all of the relaxation (two-time scale) type and our work provides a useful and simple theoretical framework for future experiments on chemical waves. This work has been published in the Journal of Chemical Physics (Ref. 132).

7. Reactions of Excited Species

We are studying the reactions of photo-excited NO_2(488 nm) with cyclo-propane and ethylene. In each case we are following the rate of the reaction by measuring the rate of disappearance of NO_2 and measuring the rate of appearance of reaction products. In the case of the reaction of NO_2 with cyclopropane, one of the reaction products is ethylene. Thus the problem is complicated by the fact that this first product further reacts with photo-excited NO_2 and we are working on the problem of unraveling the separate reaction rates.

8. Franck-Condon Approximation in Chemical Dynamics

We have applied the Franck-Condon approach for the estimation of reaction cross sections of certain cases of electronic transitions (spin-flip and quenching of electronic excitation in a collision). The theory yields correct trends and at times quantitative agreement with either exact calculations or experiments with only very simple calculations. This work has been published in the Journal of Chemical Physics.

We are finishing two other studies on Franck-Condon approaches. In the first we provide a simple prescription of construction of quasi-adiabatic energy surfaces from a given LEPS adiabatic surface and then proceed to make only the Franck-Condon approximation and none other. Thus we calculate numerically the wave functions in one channel corresponding to reactants and in the other channel corresponding to products, and take the overlap integral for a calculation of reaction transition probability. We find that the calculation is not very sensitive to the precise choice of quasi-adiabatic surface, reproduces exact calculations qualitatively and frequently quantitatively, and also checks closely with calculations in which both the Franck-Condon approximation, as well as a series of other simplifications, have been made. In the second study we turn to an investigation of angular distributions of reaction products as calculated by a Franck-Condon approximation.

The predicted angular distribution depends on the strength of the asymmetry of the interaction potential which leads to reaction and on the degree of kinematic coupling (of diagonal terms in the interaction Hamiltonian due to rotations). We compare our results with prior calculations and experiments and show that with further simplifications it is possible to introduce reduced variables with which different chemical reactions can be compared on a common basis. Both studies are being written up for publication in the Journal of Chemical Physics (Refs. 148, 149).

9. Kinetic Instabilities and First-order Phase Transitions

We have investigated the kinetics of first-order phase transitions and find that after initial nucleation instabilities may appear in the aging stage of the phase transition, such that macroscopic structures may be formed. In prior work we have shown that such structures do in fact arise in experiments in which no gradients are present (no gradients of concentration or temperature or external forces such as the gravitational field). We present both a deterministic and statistical analysis of the problem. The essential autocatalysis necessary for the instability to occur is simply related to the fact that a large particle (as in the phase transition leading to crystallization) is more stable than a small particle due to surface free energy terms. We perform a linear stability analysis of the kinetic equations and diffusion terms

and show that the expected wavelength of the pattern to be formed is in reasonable agreement with experiment. An article on this work has been accepted for publication in the Journal of Chemical Physics (Ref. 135).

INVITED LECTURES

University of California, L.A.	Distinguished Lecture Series - Three lectures on Instabilities: "Efficiency of Chemical Reactions" "Kinetics of First-Order Phase Transitions" "Chemical Dynamics"
California Institute of Technology	"Chemical Instabilities"
Environmental Protection Agency	"Modelling and the Scientific Method"
Ray Chem. Industries	"Chemical Instabilities"
Central Research Laboratories of DuPont	"Chemical Instabilities"
West Coast Conference on Chemical Dynamics	"Review of Theory of Chemical Reactions"
University of Kyushu, Japan	"Kinetics of First Order Phase Transitions"
International Conference on Nonlinear Statistical Mechanics, Kyoto, Japan	"Chemical Instabilities"
International Conference on Chemical Instabilities, Bordeaux, France	"Chemical Instabilities"
75th Anniversary of the Founding of the Laboratory of Physical Chemistry at M.I.T.	"Trends in a Lively Science"
XVIIth Solvay Conference Brussels, Belgium	Contributed Remarks

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Recent progress is reported on hydrodynamic instabilities in binary fluids heated in a gravitational field from above and below; in the thermodynamic and stochastic formulation of stability in reactive systems far from equilibrium; in the statistical mechanics of stationary states; in the theory of unimolecular reactions; in the Franck-Condon approximation in chemical dynamics; in kinetic instabilities in first order phase transitions; and in experiments on reactions of excited species.

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